Perturbation Theory: $\mathbb{H}\Psi = \mathbb{E}\Psi$ where $\mathbb{H} = H + \lambda V$

Known solution $H\psi_n = E_n\psi_n$

perturb

Parameter: $0 \to 1$

Find Taylor series expansion for $\mathbb{E}$

$$\mathbb{E} = \mathbb{E}_0 + \lambda \mathbb{E}_1 + \lambda^2 \mathbb{E}_2 + \dots$$

is some unperturbed energy E_n with eigenfunction ψ_n

$\langle \psi_n | V | \psi_n \rangle$

$$\sum_{m \neq n} \frac{|\langle m|V|n\rangle|^2}{E_n - E_m}$$

Problem: if H has degeneracy then this term may be zero... if $\mathbb{E}_2$ is infinite $\mathbb{E}_1$ is meaningless

Solution requires $\langle m|V|n\rangle = 0$ if $E_n - E_m = 0$ but that will not generally be true - we must make it true by redefining the states (wavefunctions) that are degenerate.

words: degenerate subspace : the space spanned by ψ_n and its degenerate wavefunctions.

In the H atom all the states with the same value of n are degenerate as E does not depend on l m

eg $n=3$: 3s, 3p (for $m=1,0,-1$), 3d (for $m=2,1,0,-1,2$)

These $1+3+5=9$ states are degenerate

If we want to determine how these states are changed in the presence of electric field we need to find a new basis (made up of linear combo of the above states) that has the property

$$\langle \alpha | V | \beta \rangle = 0$$

these are our new basis states in contrast to the original set [2s, 3p ($m=1,0,-1$), etc] which we will label i, j, k etc

Summary: A subset of the original unperturbed wavefunction $\psi_n = |n\rangle$ are degenerate (ie same E) which generally results in $\mathbb{E}_2 = \infty$ which means $\mathbb{E}_1$ is nonsense. The solution is to find a new set of states by a linear combo of the degenerate $|n\rangle$. These new states will still be degenerate but we aim to make them so that $\langle\alpha|V|\beta\rangle = 0$ which keeps $\mathbb{E}_2$ finite.

One way to do this is by making the states $|\alpha\rangle$ from an eigenvector of the matrix $\langle i|V|j\rangle = V_{ij}$

if $|\alpha\rangle = \sum c_i |i\rangle$ where $\begin{bmatrix} V_{ij} \end{bmatrix}\begin{bmatrix} c \end{bmatrix} = E_\alpha \begin{bmatrix} c \end{bmatrix}$

and $|\beta\rangle = \sum d_i |i\rangle$ where $\begin{bmatrix} V_{ij} \end{bmatrix}\begin{bmatrix} d \end{bmatrix} = E_\beta \begin{bmatrix} d \end{bmatrix}$

Then $\langle\alpha|V|\beta\rangle = \sum_{i,j} c_i^* \langle i|V|j\rangle d_j = E_\beta \sum_i c_i^* d_i = 0$

if $E_\alpha = E_\beta$ no help

as eigenvectors with different eigenvalues are orthogonal

actually "Gram-Schmidt" says with a bit of work this case can also be made orthogonal - see p 440

Note: under these conditions first order

$\mathbb{E}_1 = \langle\alpha|V|\alpha\rangle = E_\alpha \sum c_i^* c_i = E_\alpha$

So first order correct are these eigenvalues

Another way to achieve $\langle\alpha|V|\beta\rangle = 0$ is to find a third operator Q such that $[H,Q]=0$
$[V,Q]=0$

if $[H,Q]=0$ we can select ψ_n to be eigenfunctions of Q & H: $H\psi_n = E_n\psi_n$
$Q\psi_n = q_n\psi_n$

then: $0 = \langle i|[V,Q]|j\rangle = \langle i|V q_j|j\rangle - \langle i|q_i V|j\rangle$

$= (q_j - q_i)\langle i|V|j\rangle$

So if $q_j \neq q_i$ $\langle i|V|j\rangle = 0$

Example: Stark Effect $(V=z)$ for the 9 degenerate states of $n=3$ H-atom

$|l\,m\rangle$: $|0\,0\rangle$ (1), $|1\,1\rangle$ (2), $|1\,0\rangle$ (3), $|1\,{-1}\rangle$ (4), $|2\,2\rangle$ (5), $|2\,1\rangle$ (6), $|2\,0\rangle$ (7), $|2\,{-1}\rangle$ (8), $|2\,{-2}\rangle$ (9)

Using Mathematica we find the 9×9 matrix $\langle i|z|j\rangle$ and its eigenvalues/vectors

values: $-9,\ 9,\ -9/2,\ -9/2,\ 9/2,\ 9/2,\ 0,\ 0,\ 0$

vectors:
$(\sqrt{2}, 0, \sqrt{3}, 0, 0, 0, 1, 0, 0) \leftarrow m=0$
$(\sqrt{2}, 0, -\sqrt{3}, 0, 0, 0, 1, 0, 0) \leftarrow m=0$
$(0, 0, 0, 1, 0, 0, 0, 1, 0) \leftarrow$ ~~m=0~~ $m=-1$
$(0, 1, 0, 0, 0, 1, 0, 0, 0) \leftarrow m=1$
$(0, 0, 0, -1, 0, 0, 0, 1, 0) \leftarrow m=-1$
$(0, -1, 0, 0, 0, 1, 0, 0, 0) \leftarrow m=1$
$(0, 0, 0, 0, 0, 0, 0, 0, 1) \leftarrow m=-2$
$(\frac{-1}{\sqrt{2}}, 0, 0, 0, 0, 0, 1, 0, 0) \leftarrow m=0$
$(0, 0, 0, 0, 1, 0, 0, 0, 0) \leftarrow m=+2$

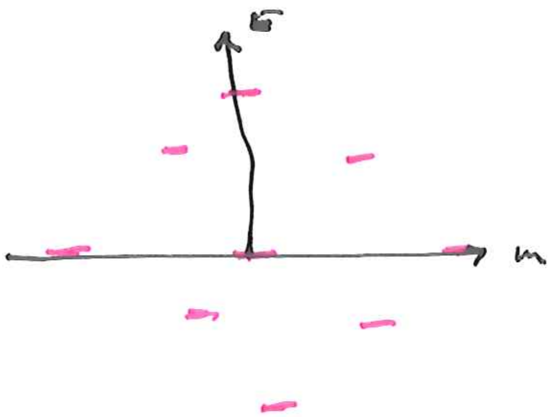
putting things together : $m=0$ $-q,\ q,\ 0$

$m=-1$ $-q/2,\ +q/2$

$m=+1$ $-q/2,\ +q/2$

$m=-2$ 0

$m=2$ 0



Note: There are for example 3 states with eigenvalue $=0$ we are not guaranteed those satisfy $\langle\alpha|V|\beta\rangle=0$

BUT these 3 states have different m values

& $[L_z, H]=0$ $[L_z, V]=0$ so the different "q" values guarantees $\langle\alpha|V|\beta\rangle=0$

Note: you can just do the dot products with the 3 $m=0$ vectors and see they are orthogonal (but not normalized yet)